

*Evaluation of Laser-Induced Breakdown  
Spectroscopy (LIBS) for the Elemental Profiling  
of Forensic Evidence*

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Thesis submitted in fulfilment of the requirements for the  
Degree of Doctor of Philosophy in Applied Science

University of Canberra

September 2014

# Abstract

Laser-induced breakdown spectroscopy (LIBS) is an emerging atomic emission based solid sampling technique that has many potential forensic applications. The work presented in this dissertation was aimed at evaluating a range of elemental profiling methods for forensic applications, with a particular focus on LIBS to determine whether this emerging technique can be readily applied to various forms of forensic evidence. In this study, the analytical performance of a commercially available LIBS instrument was evaluated for the elemental profiling of glass, paper, writing ink, inkjet ink, toner, and *Cannabis* plant material. Different reference standard matrices, which have similar compositions to the selected sample types, were used to calibrate, develop and optimise the analytical methods, taking into consideration accuracy, limits of detection and precision.

Firstly, the LIBS instrument was evaluated for the determination of elemental composition of twenty window glass samples including 14 laminated samples and 6 non-laminated or non-specified samples collected from crime scenes in the Canberra region, Australia. Three standard reference materials (NIST 610, 612, and 1831) were used to assess LIBS figures of merit. The discrimination potential of LIBS for the analysis of architectural window glass samples was compared to that obtained using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), X-ray microfluorescence spectroscopy ( $\mu$ XRF), and scanning electron microscopy energy dispersive X-ray spectrometry (SEM-EDX). The results showed that, based on the sample set chosen, the elemental analysis of window glass by LIBS provides a discrimination power greater than 97% (> 98% when combined with refractive index data), which was comparable to the discrimination powers obtained by LA-ICP-MS and  $\mu$ XRF.

Document examination is an important forensic discipline, and the legal system regularly needs the knowledge and skills of the scientific expert when questioned documents are involved in criminal or civil matters. Therefore, the evaluation of the analytical performance of LIBS was also conducted on office papers, writing inks, inkjet inks and laser printer toners, which are commonly encountered in forensic casework. The paper sample set analysed in the current thesis consisted of 32 Australian paper specimens originating from the same plant/mill but representing different brands and/or batches. In addition, a total of 131 ink or toner samples were examined that included black and blue ballpoint inks, black inkjet inks, and black laser printer toners originating from several manufacturing sources, models and/or batches. Results

from the LIBS method were then compared against those obtained using more established elemental profiling methods such as LA-ICP-MS and  $\mu$ XRF. LIBS demonstrated detectable and significant differences between different batches of the same brand as well as between different brands of paper, ink and toner samples; and provided comparable discrimination powers for the selected sample sets when compared to those obtained using LA-ICP-MS and  $\mu$ XRF (discrimination of  $\sim 98.4 - 99.8\%$ , depending on the sample subset under examination).

Finally, the analytical performance of LIBS, as well as that of ICP-MS, LA-ICP-MS and  $\mu$ XRF, was evaluated for the ability to conduct elemental analyses on *Cannabis* plant material, with a specific investigation of the possible links between hydroponic nutrients and elemental profiles from associated plant material. No such study has been previously published in the literature. Good correlation among the four techniques was observed when the concentrations or peak areas of the elements of interest were monitored. The study demonstrated that ICP-MS, LA-ICP-MS and LIBS are suitable techniques for the comparison of *Cannabis* samples from different sources, with high discriminating powers being achieved. In addition, for *Cannabis* samples collected at the same growth time, the elemental profiles could be related to the use of particular commercial nutrients.

Different methods of data analysis were performed over the source of this study in order to investigate relative discrimination powers. The data analysis approach employed was first directed at identifying a set of emission lines, elements and/or isotopes, depending on the applied analytical method and the sample type, and then constructing a set of elemental ratios. The comparison of selected elemental ratios was performed by utilizing a 2- or 3-sigma match criterion (mean value  $\pm 2$  or 3 times the standard deviation). Principle component analysis (PCA) was then employed as a second layer of discrimination, in an attempt to reduce the number of variables and to cluster samples into groups. Finally, an analysis of variance (ANOVA) and Tukey's honestly significant difference (HSD) post hoc test at a 95% confidence limit was employed for the remaining indistinguishable pairs.

Overall, it was demonstrated that LIBS is an excellent tool for the elemental profiling of matrices such as glass, paper, writing ink, inkjet ink, laser toners and *Cannabis* plant material. LIBS displayed good sensitivity and reproducibility. When combined with ease of use, fast analysis times, and low cost, the findings support the incorporation of the LIBS technique into operational forensic laboratories for the elemental analysis of a range of different evidence types.

# Acknowledgments

This dissertation would have never been written, much less completed, without the assistance of many persons to whom I am sincerely indebted.

First and foremost I would like to acknowledge God's favours on me, as He is always there and his blessings are always overwhelming me.

In acknowledgment of my feelings of obligation, regard and gratitude to my supervisory panel: Professor Chris Lennard, Dr Simon Foster, Professor James Robertson from the University of Canberra and Dr Naomi Speers from the Australian Federal Police (AFP), I would like to emphasise my indebtedness to their guidance and support throughout this journey. I especially would like to thank Professor Chris Lennard for his indispensable role in sustaining and promoting my endeavours. His efforts in the crystallization of each phase of the work contributed to my ability to pull through difficulties. I owe him the intellectual guidance, enriching observations and the moral sustenance. Throughout, he never spared any effort to provide me with the assistance and reassurance I needed to persevere in my undertaking. He was always available and willing to help me during the several setbacks encountered during the course of writing.

I have to personally thank Kylie Jones, from the AFP, who provided me with the paper, inkjet ink and toner samples analysed in this research. I would also like to thank Dr Stephen Eggins and Leslie Kinsley at the Australian National University (ANU) for their assistance during the LA-ICP-MS analyses undertaken in this study. Thanks also go to all the W J Weeden Scholarship sponsors for granting me the opportunity to undertake this research and to all staff and colleagues at the National Centre of Forensic Studies (NCFS) for providing me with such a great and friendly environment.

Needless to say, I am indebted and grateful, as always, to the unflinching and unfailing help, encouragement, and support of my family, especially my mother, to whom I dedicate every success.

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# Abbreviations

<b>AAS</b>	Atomic absorption spectroscopy
<b>ACTGAL</b>	The ACT Government Analytical Laboratory
<b>AES</b>	Atomic emission spectroscopy
<b>AFP</b>	The Australian Federal Police
<b>ANOVA</b>	The analysis of variance
<b>ANU</b>	The Australian National University
<b>ASAP</b>	An Automated Standardless Analysis Protocol
<b>ASTM</b>	The American Society of Testing and Materials
<b>ATR</b>	Attenuated total reflectance
<b>CBN</b>	Cannabinol
<b>CE</b>	Capillary electrophoresis
<b>CIJ</b>	Continuous inkjet
<b>CL</b>	Confidence limit
<b>DOD</b>	Drop-on-demand
<b>DP</b>	Discrimination power
<b>DRC-ICP-MS</b>	Dynamic reaction cell inductively coupled plasma mass spectroscopy
<b>DRIFTS</b>	Diffuse reflectance infrared Fourier transform spectroscopy
<b>EAWG</b>	The Elemental Analysis Working Group
<b>EC-ICP-MS</b>	External calibration inductively coupled plasma mass spectrometry
<b>EDX-XRF</b>	Energy dispersive X-ray fluorescence spectroscopy
<b>FAAS</b>	Flame atomic absorption spectroscopy
<b>FDE</b>	Forensic document examiner
<b>FTIR</b>	Fourier transform infrared spectroscopy
<b>GC-FID</b>	Gas chromatography-flame ionization detection
<b>GF-AAS</b>	Graphite furnace atomic absorption spectroscopy
<b>GLM</b>	General Linear Model
<b>GRIM</b>	Glass Refractive Index Measurement
<b>GW</b>	Ground wood
<b><i>HA</i></b>	The alternate hypothesis
<b><i>H<sub>o</sub></i></b>	The null hypothesis
<b>HP</b>	Hewlett-Packard
<b>HPLC</b>	High performance liquid chromatography
<b>HR-SF-ICP-MS</b>	High resolution sector field inductively coupled plasma mass spectroscopy
<b>HSD</b>	Honestly significant difference

<b>IMS</b>	Ion mobility spectrometer
<b>IRE</b>	An internal reflectance element
<b>IRMS</b>	Stable isotope ratio mass spectrometry
<b>LA-ICP-MS</b>	Laser ablation inductively coupled plasma mass spectrometry
<b>LA-ICP-OES</b>	Laser ablation inductively coupled plasma optical emission spectrometry
<b>LDA</b>	Linear discriminant analysis
<b>LDI-TOF-MS</b>	Laser desorption ionization-time-of-flight secondary ion mass spectrometry
<b>LIBS</b>	Laser-induced breakdown spectroscopy
<b>LODS</b>	Limits of detection
<b>MDLs</b>	The method detection limits
<b>m/z</b>	Mass-to-charge
<b>NAA</b>	Neutron activation analysis
<b>Nd:YAG</b>	Neodymium-doped yttrium aluminium garnet
<b>NIST</b>	The National Institute of Standards and Technology
<b>OES</b>	Optical emission spectroscopy
<b>PCA</b>	Principle component analysis
<b>PFA</b>	polytetrafluoroacetae
<b>PIGE</b>	Particle induced gamma X-ray Emission
<b>PIXE</b>	Particle-induced X-ray emission
<b>ppb</b>	Parts-per-billion
<b>ppm</b>	Parts-per-million
<b>Py-GC-MS</b>	Pyrolysis-gas-chromatography coupled with mass spectrometry
<b>R<sup>2</sup></b>	Correlation coefficient
<b>RA</b>	Reflection-absorption
<b>RI</b>	Refractive index
<b>RSD</b>	Relative standard deviation
<b>SD</b>	Standard deviation
<b>SEM-EDX</b>	Scanning electron microscopy with energy-dispersive X-ray microanalysis
<b>STR</b>	Short tandem repeat
<b>SRMs</b>	Standard reference materials
<b>SR-XRF</b>	Synchrotron radiation X-ray fluorescence spectrometry
<b>TAPPI</b>	The Technical Association of the Pulp and Paper Industry
<b>THC</b>	Delta-9-tetrahydrocannabinol
<b>TLC</b>	Thin-layer chromatography
<b>TMP</b>	Thermo-mechanical pulp
<b>TOF-SIMS</b>	Time-of-flight secondary ion mass spectrometry

<b>TXRF</b>	Total reflection X-ray fluorescence
<b>UNODC</b>	The United Nations Office on Drugs and Crime
<b>UV</b>	Ultraviolet
<b>UV-VIS</b>	Ultraviolet-visible spectroscopy
<b>WDX-EPMA</b>	Wavelength-dispersive electron probe microanalysis
<b>WDX-XRF</b>	Wavelength-dispersive X-ray fluorescence
<b>XRD</b>	X-ray diffraction
<b>μXRF</b>	Energy dispersive micro-X-ray fluorescence spectrometry